Supporting Information for

Spin Crossover in Fe(II) Complexes with N₄S₂ Coordination

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Figure S1. Supramolecular interactions in the crystal structure of 1. Chains of complexes 1 run parallel to the \( b \) axis. (a) Intraribbon embraces are observed between the thiocyanate groups of one molecule and the ethylene backbone of the next molecule. (b) View down the \( b \) axis showing interribbon interactions between the terminal thiocyanate S atom on one chain and a pyridine CH group on an adjacent chain. The intraribbon Fe…Fe distances are 9.932(8) Å and 9.851(3) Å and the closest interchain Fe…Fe distance is 8.503(8) Å and 10.685(3) Å for the 90 K and 230 K structures, respectively.

Figure S2. Supramolecular interactions in the crystal structure of 3. Chains of complexes 3 run parallel to the \( b \) axis. (a) Intraribbon embraces are observed between the BC unit of cyanoborohydride groups of one molecule and the ethylene backbone of the next molecule. (b) View down the \( b \) axis showing interribbon interactions between the terminal BH\(_3\) group on one chain and a pyridine CH group on an adjacent chain. The intraribbon Fe…Fe distance is 7.969(9) Å and 8.093(5) Å and the closest interchain Fe…Fe distance is 9.053(9) Å and 9.191(5) Å and for the 150 K and 295 K structures, respectively.
Variable-field Mössbauer spectroscopy measurements for complex 3

At 4.2 K, the Mössbauer spectrum recorded for 3 consists exclusively of a single component, whose parameters are essentially identical to those observed for the diamagnetic, low-spin (LS) Fe\textsuperscript{II} sites in 1 and 2. To confirm the presence of only diamagnetic Fe centers at this temperature, we have also recorded and analyzed a series of field-dependent spectra, which demonstrate the presence of a singlet, $S = 0$ ground state for 3. Figure S2 (bottom) shows the 4.2-K, 8-T spectrum of 3 featuring a hyperfine splitting pattern that is characteristic of a diamagnetic, $S = 0$ ground state.
Figure S5. Temperature dependence of $\chi T$ for $\alpha$-2 measured during rapid cooling (10 K min$^{-1}$) from 300 to 70 K followed by relaxation at 70 K for 8 h.

Figure S6. Temperature dependence of the $\chi T$ product obtained for polycrystalline $\alpha$-2 dispersed in hexadecane. The sample was initially flash-cooled to 40 K and subsequently measured in sequential cooling and warming cycles at 0.4 K min$^{-1}$. 
Figure S7. Temperature dependence of $\chi T$ for 3 measured in cooling mode in dark (Δ) and in warming mode after irradiation with 650-nm light at 10 K (Δ).